

## VERIFICATION OF MATHEMATICAL MODELS FOR CALCULATION OF VISCOSITY OF MOLTEN OXIDE SYSTEMS

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The subject of this work is the comparison of numerically obtained values of dynamic viscosity using different types of mathematical models and experimentally measured data of viscosity of oxide systems. The ternary system of  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ , which presents simplified base of the casting powders used in technological process, was submitted to the experiment. Experimental research of dynamic viscosity is highly limited by its complexity. That's why model studies play such an important role in this field. For mathematic calculation of viscosity the NPL model, Iida model and Urbain model were chosen. The results of simulation were compared with the experimentally obtained values of viscosity.

**Key words:** mathematical modelling, viscosity, oxide melts

### INTRODUCTION

Viscosity is one of the most important physical-chemical properties in the case of metallurgical melts, in view of its direct effect on the kinetic conditions of the processes, and it is one of the key factors to be taken into consideration in process modelling. Viscosity of slags is a complex function of the slag composition, temperature and internal structure.

The difficulty and high cost of measuring the viscosity of slags has led to development of numerous viscosity models. Most of the models are applicable to the relatively limited composition and temperature ranges.

Development of reliable and accurate general model that would enable prediction of the viscosities of slag systems over a wide range of compositions and temperatures is very important for a number of industrial processes. Numerous authors have already dealt with determination or verification of mathematical models for calculation of viscosity. Riboud [1] has developed a model, which expresses the activation energy as the linear addition of the network-forming components, but this does not reflect the non-linear variation of activation energy with composition. The Urbain model [2] assumes the Weymann-Frenkel relation. It expresses the activation energy dependence on composition as a polynomial expression of composition containing three parameters, but many parameters are adopted with fewer structural factors. Models by Iida and NPL model – Mills and Sridhar [3] are based on the optical basicity. The structural model by Du et al. [4] does not consider the real existing struc-

tural units, whereas for example Zhang [5] takes into account concentrations of bridging, non-bridging and free oxygen ions in the given structure.

This article gives a comparison of three mathematical models for calculation of viscosity of oxide systems. Individual models were verified with use of experimental data.

### EXPERIMENT

The ternary system  $\text{CaO - Al}_2\text{O}_3 - \text{SiO}_2$  was selected for the experimental study. A concentration series with the addition of 3; 6; 9; 12 and 15 wt.% of  $\text{SiO}_2$  was prepared for an assessment of the influence of  $\text{SiO}_2$  concentration on the oxide system viscosity. Its chemical composition is shown in Table 1.

Table 1 **Chemical composition of the concentration series / wt. %**

	$\text{SiO}_2$	CaO	$\text{Al}_2\text{O}_3$
TS	47,20	36,90	15,90
TS + 3 wt.% $\text{SiO}_2$	50,20	34,80	15,00
TS + 6 wt.% $\text{SiO}_2$	53,20	32,71	14,09
TS + 9 wt.% $\text{SiO}_2$	56,20	30,61	13,19
TS + 12 wt.% $\text{SiO}_2$	59,20	28,51	12,29
TS + 15 wt.% $\text{SiO}_2$	62,20	26,41	11,39

The viscosity measurements were carried out by the rotating viscometer Anton Paar FRS 1 600. This equipment was described in detail in previous publication [6]. The viscosity was measured during heating up to 1 600 °C at the heating rate of 3,3 °C/min. The optimum shear rate of 85 rpm was chosen for viscosity measurements.

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## Mathematical models

Temperature dependences of viscosity were determined using three selected mathematical models – the NPL model, Iida model and Urbain model.

In the first stage of mathematical modelling of viscosity we used for calculation the **NPL model** developed by authors Mills and Sridhar [4]. This model includes into the calculation the structural issues of slag melts through the optical basicity, which provides information on the occurrence of bridging, non-bridging and free oxygen ions in the slag. The authors of the work [7] linked the Weymann-Frenkel equation, which describes the temperature dependence of viscosity, with the concept of optical basicity:

$$\eta = A \cdot T \cdot \exp\left(\frac{1000 \cdot B}{T}\right) \quad (1)$$

where  $A$  and  $B$  are interdependent parameters, parameter  $B$  is a function of optical basicity:

$$-\ln A = 0,2056 \cdot B + 12,492 \quad (2)$$

$$B = 297,14 \cdot \Lambda^2 - 466,69 \cdot \Lambda + 196,22 \quad (3)$$

$\Lambda$  is the optical basicity calculated according to the following relation:

$$\Lambda = \frac{\sum x_i \cdot n_i \cdot \Lambda_i}{\sum x_i \cdot n_i} \quad (4)$$

where  $x$  is molar fraction of the component  $i$  /-,  $n$  is number of oxygen atoms in molecule /- and  $\Lambda_i$  is optical basicity of the component  $i$  /-. The input data for calculation of the temperature dependence of viscosity using the given model were taken from the literature [7].

The **Iida model** was used as another model for calculating viscosity. This model is based on the Arrhenius equation [8]:

$$\eta = A \cdot \eta_0 \cdot \exp\left(\frac{E}{B_i}\right) \quad (5)$$

where  $A$  is the pre-exponential factor /s<sup>-1</sup>,  $E$  is the activation energy /J.mol<sup>-1</sup>,  $\eta_0$  is hypothetical viscosity of the oxide system /Pa.s and  $B_i$  is the basicity index /-.

This model takes into account also the complex network structure of slags by use of the basicity index  $B_i$  [9].

$$B_i = \frac{\sum (\alpha_i \cdot W_i)_B}{\sum (\alpha_i \cdot W_i)_A} \quad (6)$$

where  $\alpha_i$  is the specific coefficient /-,  $W_i$  is the mass fraction of the component  $i$  /- and indexes A or B represent acid and alkaline oxides.

It is possible to determine the pre-exponential factor  $A$  and activation energy  $E$  with use of the following temperature dependences [8]:

$$A = 1,745 - 1,962 \cdot 10^{-3} \cdot T + 7 \cdot 10^{-7} \cdot T^2 \quad (7)$$

$$E = 11,11 - 3,65 \cdot 10^{-3} \cdot T \quad (8)$$

Hypothetic viscosity was obtained with use of the equation:

$$\eta_0 = \sum \eta_{0i} \cdot X_i \quad (9)$$

where  $X_i$  is the molar fraction of the component  $i$  and  $\eta_{0i}$  is hypothetical viscosity of pure oxide, which can be determined according to the following relation:

$$\eta_{0i} = 1,8 \cdot 10^{-7} \cdot \frac{[M_i \cdot (T_m)_i]^{1/2} \cdot \exp\left(\frac{H_i}{R \cdot T}\right)}{(V_m)_i^{2/3} \cdot \exp\left[\frac{H_i}{R \cdot (T_m)_i}\right]} \quad (10)$$

where  $M_i$  is the molar mass /kg.mol<sup>-1</sup>,  $V_{mi}$  is the molar volume /m<sup>3</sup>.mol<sup>-1</sup>,  $T_{mi}$  is the melting temperature /K,  $R$  is the gas constant /J.K<sup>-1</sup>.mol<sup>-1</sup>,  $X_i$  is the molar fraction /- and  $H_i$  is the enthalpy of melting of individual component  $i$  /J.mol<sup>-1</sup>, expressed by the relation:

$$H_i = 5,1 \cdot (T_m)_i^{1,2} \quad (11)$$

In the last stage of mathematical modelling we used the **Urbain model**. This model assumes validity of the Weymann-Frenkel's equation (1). The parameters  $A$  and  $B$  are calculated with use of the following equations [10]:

$$-\ln A = 0,29 \cdot B + 11,57 \quad (12)$$

$$B = B_0 + B_1 \cdot X_G + B_2 \cdot X_G^2 + B_3 \cdot X_G^3 \quad (13)$$

where

$$B_0 = 13,8 + 39,935 \cdot \alpha - 44,049 \cdot \alpha^2 \quad (14)$$

$$B_1 = 30,81 - 117,151 \cdot \alpha + 139,998 \cdot \alpha^2 \quad (15)$$

$$B_2 = -40,943 + 234,05 \cdot \alpha - 300,04 \cdot \alpha^2 \quad (16)$$

$$B_3 = 60,762 - 153,928 \cdot \alpha + 211,162 \cdot \alpha^2 \quad (17)$$

The parameter  $\alpha$  can then be determined with use of the following relation:

$$\alpha = \frac{X_M}{X_M + X_A} \quad (18)$$

where  $X_M$  is the molar fraction of individual oxides – modifiers /- and  $X_A$  is the molar fraction of individual amphoteric oxides /-.

## RESULTS

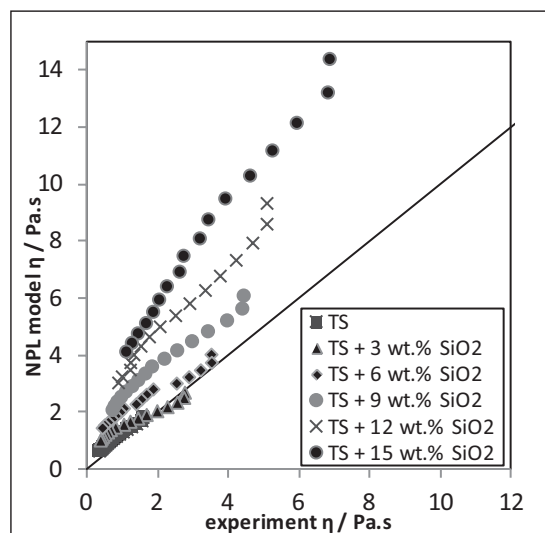
The temperature interval for calculation of viscosity was chosen in accordance with the experimentally measured values of viscosity, i.e. 1 400 °C – 1 600 °C.

Comparison of the calculated temperature dependence of viscosity using the NPL model with the experimentally measured values is shown in Figure 1.

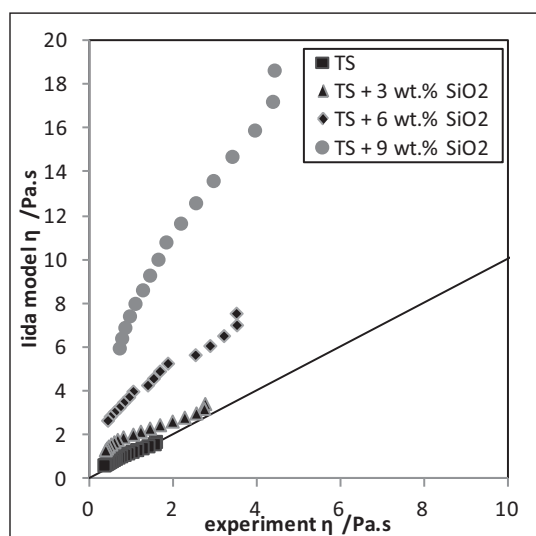
It is evident from the figure that the systems with the lower content of SiO<sub>2</sub> show the smallest deviations from the experimental values. The average deviation increased considerably with the increasing content of SiO<sub>2</sub>.

Figure 2 compares the values of viscosity calculated by the Iida model with the experimentally determined temperature dependence of viscosity for systems of the concentration series of SiO<sub>2</sub>.

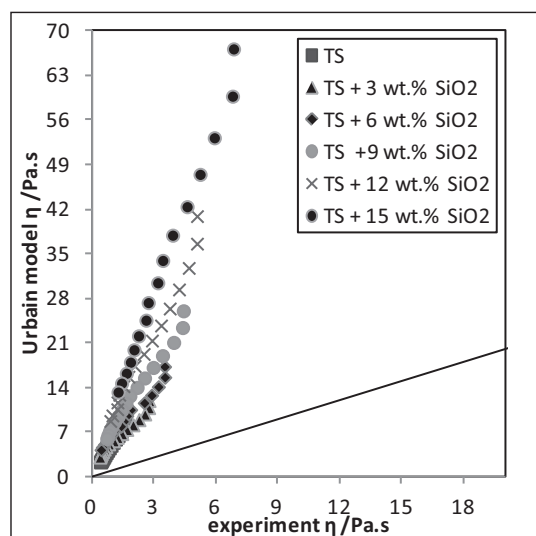
The systems with additions of 12 and 15 wt. % of SiO<sub>2</sub> were omitted from this comparison due to huge



**Figure 1** Comparison of experimentally determined values of viscosity with the values calculated with use of the NPL model



**Figure 2** Comparison of experimentally determined values of viscosity with the values calculated with use of the Iida model



**Figure 3** Comparison of experimentally determined values of viscosity with the values calculated with use of the Urbain model

deviation of the calculated values of viscosities from the experimental data. Deviation of these systems was greater than 1000 %. It is obvious from Figure 2 that the best agreement was achieved in the basic ternary system (TS). The average deviation again increased with the addition of  $\text{SiO}_2$ .

Comparison of the experimental values of viscosity and the values calculated using the Urbain model is shown in Figure 3. It was determined from these results, that this model showed large deviations even in the case of the basic ternary system (450 %). In other systems of the investigated concentration series the deviation increased with the increasing content of  $\text{SiO}_2$ , similarly as in previous models.

## DISCUSSION AND CONCLUSIONS

Viscosity in the slag systems is determined by the silicate structure - acidic slags with large polymerised ions are highly viscous, while alkaline slags with small de-polymerised silicate ions are less viscous. Mathematical modelling of viscosity is complicated not only by oxides, which polymerise or conversely de-polymerise melt, but also by the interactions between cations and anions. The functionality of mathematical models is therefore often limited by the temperature and concentration range of some components, such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , [11]

It was established on the basis of experimental measurement of the temperature dependence of viscosity of the concentration series of  $\text{SiO}_2$  from the ternary system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  that dynamic viscosity of all investigated oxide systems decreases exponentially with the increasing temperature, and that it increases with the addition of  $\text{SiO}_2$ . This fact was confirmed also by theoretical calculations performed with use of the above three mathematical models (Urbain, Iida and NPL model).

It is evident from Figures 1-3 that in all selected mathematical models the average deviation significantly increases with the addition of silicon dioxide. Only in the case of the calculated temperature dependence of the basic ternary system without the addition of  $\text{SiO}_2$  with use of the Iida model, the average deviation was lower than 50 %. On the other hand, this model had the highest deviation in the case of the ternary system with the addition of 12 and 15 wt. % of  $\text{SiO}_2$ . Comparison of all three models revealed that the NPL model showed the smallest total deviation from the experimental data.

The results of mathematical modelling of viscosity can be summarised as follows:

The above mathematical models (NPL, Iida and Urbain model) reveal an exponential decrease of viscosity with the temperature and an increase of viscosity with the increasing content of  $\text{SiO}_2$ . However, due to high average deviations, it is not appropriate to use these mathematical models for real calculations of viscosity of the ternary system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  in the concentra-

tion range of  $\text{SiO}_2$  47,2 wt. % - 62,2 wt. %, and in the temperature interval of 1 400 °C – 1 600 °C.

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**Note:** The responsible translator for English language is Ing. Boris Škandera, Ostrava, Czech Republic